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Effects of Hydration Procedures and Calcination in the Presence of NaCl on the Properties of Lime Hydrates

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ABSTRACT

This investigation is part of a study of factors that affect the properties of lime putties. The influence of salt (NaCl) content and calcining temperature on the surface area and on the reactivity of the calcinates of 1) dolomite, 2) calcium carbonate (CaCO_3), and 3) basic magnesium carbonate was studied. It was found that both the presence of NaCl and increased calcining temperatures acted to decrease the surface area and reactivity of all three materials.

The influence of NaCl content and calcining temperature of the calcinate on the plasticity of the dolomitic hydrate was investigated. Two hydration procedures were used to convert the calcinates to the hydrated form - an atmospheric pressure and a high-pressure method. The results indicate that neither the presence of NaCl nor increased calcining temperatures had any beneficial influence on the plasticity of the low-pressure hydrate. However, NaCl appears to improve slightly the plasticity of the high-pressure hydrate.

It was found that calcium hydroxide (Ca(OH)_2) was considerably coarser and of lower plasticity than magnesium hydroxide (Mg(OH)_2). Both are composed of thin hexagonal platelets.

INTRODUCTION

The addition of salt (NaCl) to CaCO_3 , before calcination, accelerates the crystal growth of the CaO and decreases its reactivity toward water, according to Noda and Kan (1937). Noda and Oka (1938) noted that the growth of MgO crystals was accelerated when NaCl was added to the carbonate before calcination.

Briscoe and Mathers (1927) reported that when dolomites naturally contained more than 0.07 percent chloride ion, a plastic hydrate was produced, whereas dolomites containing less than this amount yielded low plasticity hydrates.

Lamar and Shrode (1953) have shown that the liquid inclusions in dolomites contain Na^+ and Cl^- ions, among others.

These reported influences of sodium chloride on the properties of the components of calcined dolomite, and the fact that dolomites often contain liquid inclusions rich in NaCl, suggested that it might be of interest to measure some of the properties of the calcinates made from carbonate starting materials that contained varied amounts of NaCl added before calcination. Because plasticity is closely related to the workability of masonry mortars, the property of plasticity and the basic factors that affect it are the focus of the present study of factors influencing the properties of hydrated limes.

RAW MATERIAL SELECTION

Four hundred pounds of crushed Niagaran dolomite were kindly furnished by the Marblehead Lime Company for this study. The material had been crushed and sized at the plant. The particle-size distribution of the dolomite was:

<u>Screen</u>	<u>Weight percent</u>
+0.371 inch	10.8
-0.371 inch + 4 mesh per inch	48.2
-4 + 10 mesh	35.7
-10 + 14	3.0
-14 + 20	1.0
-20 + 28	0.3
-28	1.0

No chemical analysis of this material was made, but it is considered to be similar to samples from the same quarry analyzed previously at the Illinois Geological Survey. The following chemical analysis is taken from Lamar (1957):

SiO ₂	0.11	Na ₂ O	0.06
Al ₂ O ₃	0.30	CO ₂	47.05
Fe ₂ O ₃	0.19	Ign. loss	47.87
CaO	31.20	SO ₃	0.10
MgO	20.45	MnO	0.015

The sum of CaCO₃ and MgCO₃ is 98.45 percent, which shows that this is a rather pure stone from the industrial viewpoint. The stone was used as received with no further treatment.

The raw material sources of CaO and MgO were CaCO₃ (precipitated) and basic magnesium carbonate, respectively. Both were very fine powders. The magnesium carbonate was labeled "U.S.P., Heavy Powder, MgCO₃ Formulae Weight, 84.33," but x-ray diffraction and ignition loss proved it to be the basic MgCO₃ (5MgO · 4CO₂ · 5H₂O). The CaCO₃ was precipitated, U.S.P. (light). Its chemical analysis was given by the supplier as

SiO ₂	-	0.03
TiO ₂	-	0.09
Al ₂ O ₃	-	0.06
Fe ₂ O ₃	-	0.05
MgO	-	0.38
CaO	-	55.53
Na ₂ O	-	0.06
K ₂ O	-	0.09

The NaCl used was reagent grade crystals from Baker and Adamson.

EXPERIMENTAL PROCEDURES

Sample Preparation for Calcination

The desired amount of carbonate starting material with the same particle-size distribution as given above (1400 grams of dolomite, or 600 grams of CaCO_3 [powder] or basic MgCO_3 [powder]) was weighed into a 1500 milliliter beaker, to which was added 450 ml of distilled water containing in solution the desired amount of NaCl. This was placed on a steam bath and the water evaporated overnight. Even the samples that contained no added salt received the same pretreatment. The NaCl contents reported are in weight percent based on the uncalcined carbonate starting material.

Calcination

The pretreated samples were placed in shallow refractory saggars (4 inches high x 8 inches in diameter) to a depth of approximately three inches. Two such samples, each with the same amount of NaCl, were calcined at the same time.

A muffle-type Globar-heated furnace was used. The two saggars occupied most of the furnace's floor space, but there was 2 to 3 inches overhead clearance. A tube was inserted through the rear of the furnace into the muffle at a level of approximately one inch above the saggars. By means of this tube a slow current of air was flushed through the furnace during the entire calcination cycle. A hole in the furnace door and various other openings allowed the air to escape.

After the cold furnace had been loaded and the stream of air started, the power to the furnace was turned on. The heating rate was controlled manually so that the desired maximum temperature was reached in seven to eight hours. A platinum-platinum + 10 percent rhodium thermocouple inside a porcelain protection tube was placed two inches above the saggars for temperature measurement. The time at this maximum temperature was two hours, unless otherwise specified. After this soaking period the power was shut off and the furnace and its contents, with the air stream still on, was allowed to cool for 16 hours. The material, still at 350°C ., was removed from the furnace, immediately placed in two-quart Kerr jars, and the self-sealing lids were tightened. As the contents of the jars cooled, a vacuum was produced in the jars. These were stored until needed.

Reactivity of Calcined Carbonates with Water

To establish the reactivity of the calcined oxides with water an apparatus similar to that described by Murray, Fischer, and Sabeen (1950) was assembled. Figure 1 is a schematic drawing of this apparatus.

The function of the apparatus is to measure the temperature rise in a given amount of water when a given amount of calcinate is added. A ratio of 7 parts of distilled water to 1 part of calcinate by weight was used.

Operation is as follows: 200 grams of distilled water at 26°C is placed in the Dewar flask, the stirrer is started, the recorder is calibrated against the potentiometer, then the potentiometer is removed from the circuit and the recorder connected directly to the thermocouple in the Dewar calorimeter. Now 28.6 grams of the calcinate, ground to a powder with a mortar and pestle, is added through the powder funnel; the temperature rise of the water vs. time is recorded by the recorder. The values reported, for comparative purposes, are the temperature rises after 1000 seconds or ΔT_{1000} ; the average value of three runs is reported. The reproducibility is ± 15 percent.

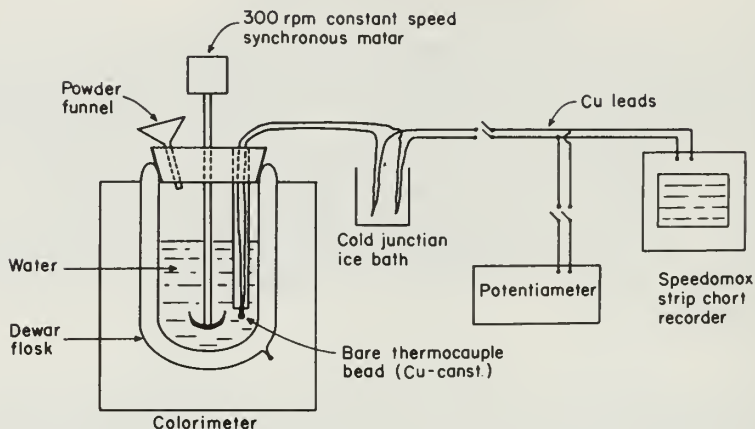


Fig. 1. - Reactivity apparatus.

Surface Area

Surface areas were determined by low temperature, low pressure adsorption of nitrogen, after the method of Brunauer, Emmett, and Teller (1938). The surface measurements of those samples having areas in excess of one m^2/g (square meters per gram) is reproducible to about ± 5 percent.

Hydration

Two means of hydrating the calcinates were used—an open-dish, atmospheric pressure method, and a closed-vessel, high-pressure method.

The operation of the atmospheric pressure method involves weighing 700 to 800 grams of the calcined stone into a 12-inch diameter evaporating dish (this calcinate has essentially the same size distribution as the uncalcined stone). Distilled water in an amount equal to 30 percent of the weight of the stone was placed in a separatory funnel, which had been previously adjusted to deliver at the rate of 7.0 ml per minute. The stone and water were stirred with a steel rod during the entire course of the hydration. The maximum temperature of the calcinate-water mixture (the "bed" temperature) was observed by stirring at frequent intervals with a thermometer. After all the water had been added, the moist mixture was placed in an open, two-quart Kerr jar, which was set in an oven and dried for 16 hours at 105°C .

After the drying period, a self-sealing Kerr lid was tightened on the jar, and after cooling to room temperature the hydrate was ball-milled in a two-gallon porcelain mill for one hour. The milled material was returned to the Kerr jar for storage.

After considerable experimentation with various setups in an attempt to hydrate the calcined dolomite almost completely, the apparatus shown in figure 2 was finally used for all pressure hydrations unless otherwise specified.

The procedure used for the pressure hydration of the calcined dolomite was as follows: 625 grams of calcined solids, having roughly the same particle size as the original stone, were weighed into the inner can and the bomb was closed and placed in a cold oven. A vacuum was drawn on the bomb through the release

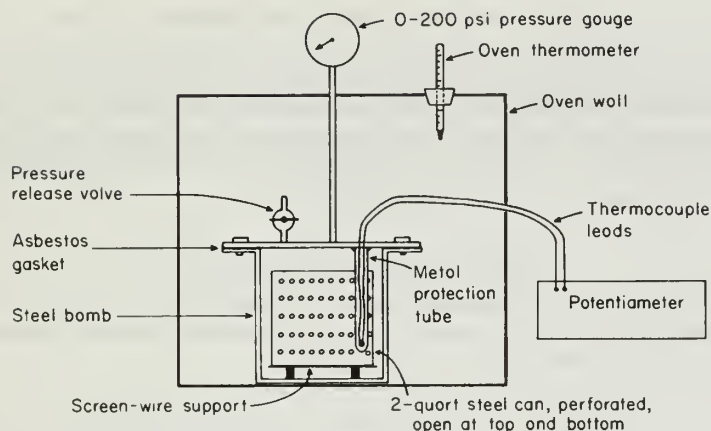


Fig. 2. - Pressure hydration apparatus.

valve and 475 ml of water (2.8 times the theoretical amount necessary for complete hydration) was drawn in on top of the calcined stone. The valve was closed and the oven turned on. In about three hours the pressure in the bomb rose to 140 psi gauge (the maximum pressure of all hydrations unless otherwise specified). This pressure was maintained for 4 1/2 hours. The release valve was then opened and the pressure became atmospheric. The bomb was then opened and its contents dried in a two-quart jar at 105°C for 16 hours. After drying, a self-sealing lid was tightened on the jar. This material was then ball-milled for one hour.

In the hydration of CaO and MgO samples, the procedure described above was followed, except that 200 grams of solids and four times the amount of water necessary for complete hydration of the oxide were used.

Plasticity Determinations

The visco-plastic properties of the hydrate pastes or suspensions were explored by means of the conventional Emley plasticimeter. This apparatus was constructed at the Geological Survey after A.S.T.M. specifications (1949). Porcelain base plates were used. The plates were made in the University of Illinois Ceramic Engineering Department to conform to the prescribed absorption rates. The plasticity determinations were made according to the standard procedures described by the A.S.T.M. method C-110-49. The plasticity was determined immediately after tempering with water and again after soaking for 24 hours. The water at standard consistency, as given in the text, is the weight percent of water in the total water-solid mixture necessary to produce a paste of standard penetration on the penetrometer (standard consistency).

In most cases only one determination of plasticity was possible, due to the lack of hydrate. Where duplicate runs were made, the reproducibility was within ± 15 percent of the average value.

Drying of Soaked Hydrates

In order to study the hydrates after they had been soaked, to see what alterations had taken place during soaking, it was necessary to dry the samples in such a way as to minimize any alteration caused by the drying itself. The method used to dry the sample is similar to that given by Wells and Taylor (1937).

After the Emley value of the soaked paste was determined, a 75-gram sample of the wet putty was placed in 150 ml of absolute ethanol and shaken for several minutes. The sample was then transferred to a Buchner vacuum filter, the liquid removed by suction, and the cake washed with ethanol and ethyl ether. The nearly dry cake was placed in a vacuum desiccator, which was continually pumped for 24 to 48 hours to remove the last ethanol and ether. The dried samples were studied by various techniques, as will be described.

Carbon Dioxide Determinations

The method used to determine carbon dioxide depended on the acid evolution of the CO_2 with adsorption on ascarite. The procedure and apparatus are similar to those given by Hillebrand and Lundell (1953).

Ignition Loss and Composition Estimation

The ignition loss was determined by heating weighed samples in platinum crucibles to 975°C for two hours.

From the ignition loss of the dolomitic hydrate the composition of the hydrate was calculated. The calculations were based on the assumptions that all the CaO had been hydrated in the hydration process, that there was no carbonation of the hydrate, and that the original dolomite had the theoretical dolomite composition. The validity of these assumptions was checked.

The first assumption is widely accepted because CaO hydrates so readily. A rough check of this assumption comes from an examination of the x-ray powder patterns of the hydrates which never showed any CaO lines. The validity of the second assumption was checked by determining the CO_2 content of some hydrates. It was found to be less than one percent (tables 6, 7). A theoretical dolomite, $\text{CaMg}(\text{CO}_3)_2$, contains 21.9 percent MgO and 30.4 percent CaO . The chemical analysis given previously, which is assumed to represent the stone used here, showed 20.45 percent MgO and 31.2 percent CaO . For our purposes this is a rather close approach to the theoretical composition of dolomite.

It is evident that the compositions of the hydrates calculated from the ignition loss are not highly accurate, and it is estimated that the amount of any component reported may be in error by at least ± 3 percent of the reported value.

X-Ray Identifications

All x-ray diffraction powder patterns were made on a G. E. XRD-3, Recording Spectrometer, with $\text{Cu K}\alpha$ radiation. A shallow Al sample holder was used. The powdered samples were placed in the holder and smoothed off with a glass slide.

Particle-Size Analysis

The particle-size distribution of some of the hydrates was determined by dispersing the hydrate in anhydrous n-butanol in a thermostatted cylinder and withdrawing portions at intervals. Anhydrous n-butanol was used on the recommendation of Bishop (1939). The portions were evaporated to dryness and the weight of the dry residue was determined. X-ray diffraction patterns of these residues were made.

Water Retention of the Hydrates

It was observed, in the Emley plasticity test, that those limes that appeared moist for the longest time always had the highest plasticity values. It was therefore thought desirable to make a measurement that would reflect the water-retention ability of the lime putties and substantiate the visual observations of water retention in the Emley test.

Pelaez and Murray (1956) devised a penetration test to measure water retention. With a penetrometer they measured the thickness of nonpenetrable cake built up on a vacuum filter as a function of time of evacuation. They found that the tendency to retain water was in a linear relationship to the Emley plasticity. The more tenaciously a lime clings to the water in the paste, the greater is its Emley plasticity.

Rather than measure the penetration of a filter cake, the apparatus shown in figure 3 was set up so that the volume of water removed from the lime putty as a function of time could be measured directly.

The sample of hydrate was tempered with water to the standard consistency used for the Emley determination of plasticity. With the system at atmospheric pressure, the paste was placed in the Buchner funnel that contained a moistened No. 1 Whatman filter paper, and the paste was struck off level with the rim of the funnel. The timer was started when the first

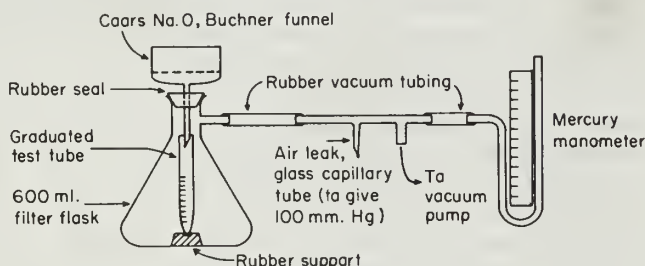


Fig. 3. - Apparatus for measuring water retention.

paste was placed in the funnel. After the funnel was filled, the vacuum pump was turned on at one minute after the first paste was placed on the funnel. In less than 0.2 minute a vacuum of 100 mm of Hg was attained. The volume of water removed was recorded as a function of time. The test was discontinued when the manometer indicated the vacuum had been lost. The loss of vacuum due to cracking of the cake or the cake pulling away from the funnel wall occurred rather abruptly (in less than one minute). The results are reported as the empirical ratio R , where:

$$R = \frac{\text{Total volume of water removed until the vacuum is lost}}{\text{Total time until vacuum is lost}} = \frac{\text{ml}}{\text{min}}$$

This term gives a rate of drying out or removal of water from the paste and will be referred to later as "the water removal factor."

Electron Micrographs

All electron micrographs were made in the Chemistry Department of the University of Illinois by A. E. Vatter. The carbon replica technique, as first described by Bradley (1954), was used. In brief, the method is as follows: a glass slide is coated with a film of collodion, then the sample is spread on the collodion film, and a film of carbon is shadowed over the specimen. Now the composite layer is floated away from the glass slide in water, then transferred to acetone where the collodion is removed. Next the sample is removed from the carbon replica by floating in dilute acid solution. The clean carbon replica is then mounted on a grid for observation. The shadowing angle was 20° .

EXPERIMENTAL RESULTS

Some Properties of the Calcined Materials

Calcined Dolomite

The treatment of the Thornton, Illinois, dolomite and the reactivity and surface area of the resulting products are shown in table 1.

It will be noted in table 1 that the samples calcined at 825°C were held at the maximum temperature for seven hours, but that at all other temperatures the retention time at the maximum temperature was fixed at two hours. The longer retention time at 825°C was necessary to complete the decarbonation of the sample, as explained below.

The results of calcining samples of Thornton dolomite containing 0.0, 1/2, and 1 percent NaCl at 825°C for two hours are interesting. X-ray diffraction patterns of these calcined samples showed lines due to CaO, MgO, and CaCO₃ but no lines due to dolomite. The intensity of the CaCO₃ lines decreased as the NaCl content increased. The ignition loss was determined on these calcinates. The sample that contained no NaCl lost 21.05 percent, the one containing 1/2 percent NaCl lost 10.17 percent, and the sample containing 1 percent NaCl lost only 5.01 percent. This indicates that under the conditions used here the NaCl greatly aided in the decarbonation of the dolomite. However, even in the presence of 1 percent NaCl not all the carbonate had been decomposed. However, after seven hours of retention at 825°C no carbonate lines could be observed in the x-ray pattern. So all samples prepared at 825°C were held for this period of time to insure complete decarbonation.

X-ray diffraction patterns of the samples calcined at 875°C and higher for a period of two hours, under conditions used here, showed no lines due to carbonate materials. Therefore, this retention period was used for all samples prepared at temperatures of 875°C and higher.

In figure 4 it will be noted that the surface area decreases with both increasing temperature of calcination and with increasing salt content. The influence of temperature on the surface area, especially in the region of 900° to 1000°C, is

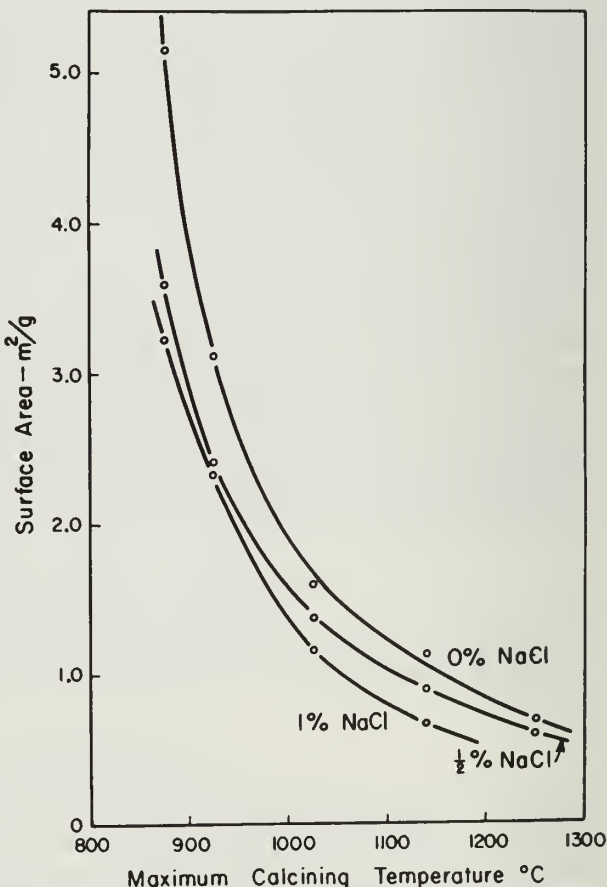


Fig. 4. - Influence of NaCl on the surface area of calcined dolomite from Thornton, Illinois. Time at maximum temperature was two hours.

Table 1. - Properties of Calcined Dolomite from Thornton, Illinois

No.	Maximum calcining temp. (°C)	Total time at max. temp. (hrs.)	NaCl added (wt. percent based on un- burned stone)	Reactivity ΔT_{1000} (°C)	Surface area (m ² /gram)
8	825	7	0	16.4	3.55
9	"	"	0.1	15.1	-
10	"	"	0.4	9.7	3.10
11	"	"	0.60	7.2	-
12	"	"	0.90	6.2	-
13	"	"	1.25	4.9	2.71
14	"	"	1.75	4.4	-
15	"	"	2.50	4.2	2.53
16	"	"	3.50	4.1	2.45
17	"	"	5.00	4.1	-
18	875	2	0	17.8	5.15
19	"	"	0.50	9.7	3.60
20	"	"	1.00	7.0	3.24
21	925	2	0	17.1	3.12
22	"	"	0.50	8.8	2.43
23	"	"	1.00	6.8	2.35
24	1025	2	0	13.0	1.62
25	"	"	0.50	8.0	1.37
26	"	"	1.00	4.0	1.17
27	"	"	2.00	3.2	-
28	"	"	3.00	2.3	-
29	"	"	4.00	2.2	1.01
30	1140	2	0	12.3	1.14
31	"	"	0.50	7.6	0.93
32	"	"	1.00	2.8	0.68
33	1250	2	0	10.5	0.69
34	"	"	0.50	7.0	0.60

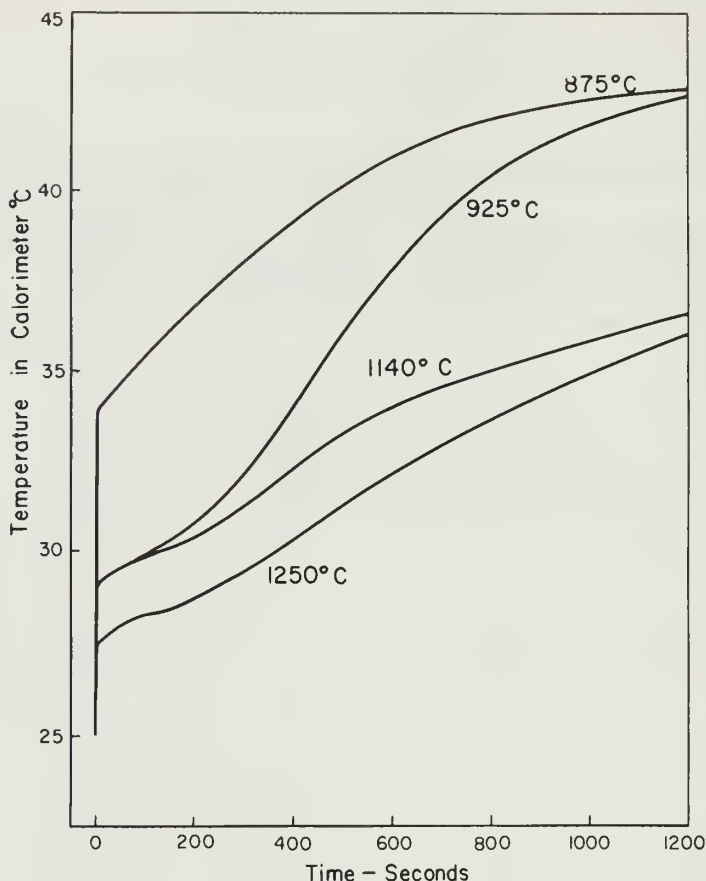


Fig. 5. - Temperature rise in calorimeter vs. time for dolomite calcined at various temperatures and containing 0 percent NaCl.

greater than that of salt. In the region of 1000° to 1200°C, 1 percent salt has approximately the same effect on the surface area as an increase in temperature of about 100°C.

Figure 5 shows some tracings of the calorimeter curves of dolomite calcined at various temperatures. At time zero, when the solids were added, the temperature instantaneously jumped 3° to 8°C, depending on the calcining temperature. In the case of those calcined at 925°C and higher, there was then a period of 100 to 150 seconds of very little activity, after which the temperature began to rise more rapidly with time. The shapes of these curves are very similar to those given by Knibbs (1937). When the calcined dolomite comes in contact with liquid water, under the conditions used here, there is an initial, very steep rise in temperature amounting to as much as 50 percent of the total rise. Knibbs calls this the initial liquid adsorption rise; the next period, of little activity, he calls the period of quiescence. Then the main reaction of the calcined dolomite and water proceeds for a considerable period of time.

With samples calcined at 875°C there is no period of quiescence, and after the initial sharp rise in temperature the reaction proceeds quite rapidly.

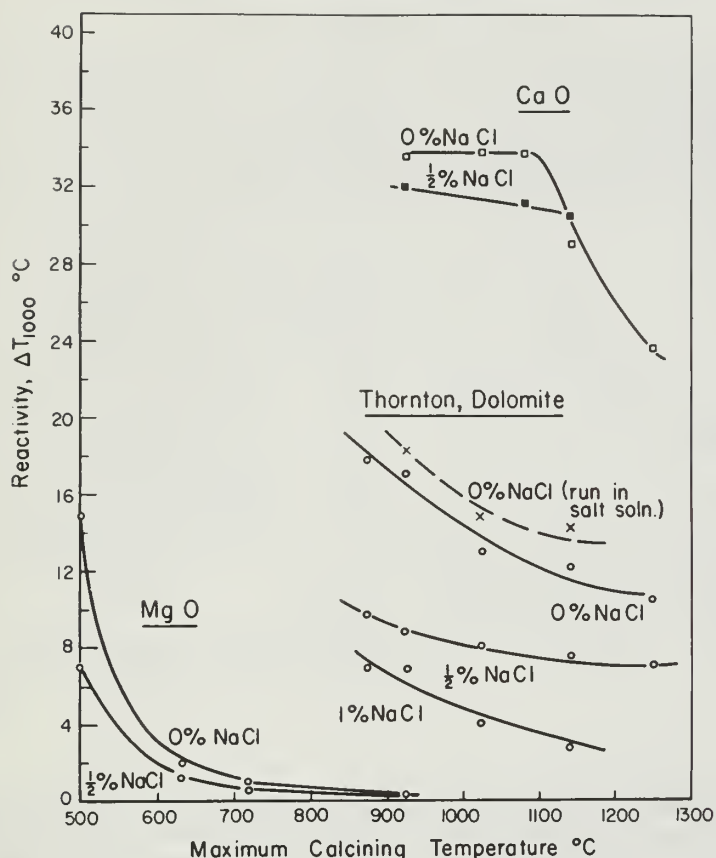


Fig. 6. - Influence of NaCl on the reactivity of CaO, MgO, and dolomite from Thornton, Illinois. Time at maximum temperature, two hours. All run in distilled water except where noted.

Figure 6 shows the influence of salt content and calcining temperature on the reactivity of CaO, MgO, and dolomite so that these materials may be compared directly. The properties of MgO and CaO are discussed later in the text. The reactivity of the MgO decreases rapidly with increasing temperature of preparation from the basic carbonate, and by 925°C its reactivity is immeasurably small on our apparatus. The addition of 1/2 percent salt decreases the reactivity at low temperatures, but its influence is very slight at the higher calcination temperatures.

The reactivity of CaO without salt is influenced only slightly by temperature of calcination up to approximately 1100°C; it then falls rather rapidly as the temperature rises. The presence of salt seems to decrease the reactivity somewhat at temperatures of less than 1100°C.

For dolomite the decrease in reactivity is continuous as the temperature of calcination increases. Salt has a very large effect on the reactivity; 1/2 percent of salt is approximately equivalent in its effect on reactivity to a 400°C increase in temperature of calcination.

Table 2. - Properties of CaO

No.	Maximum calcining temp. (°C)	Total time at max. temp. (hrs.)	NaCl added (wt. percent based on un- burned CaCO_3)	Reactivity ΔT_{1000} (°C)	Surface area (m^2/gram)
35	825	7	0	33.8	4.42
36	"	"	0.50	29.7	0.66
37	"	"	1.0	29.3	-
38	"	"	2.0	28.4	-
39	"	"	3.0	25.9	0.51
40	"	"	4.0	27.2	-
41	"	"	5.0	-	-
42	925	2	0	33.5	3.70
43	"	"	0.50	32.0	1.04
44	1025	2	0	33.8	1.29
45	"	"	0.50	30.4	0.62
46	1080	2	0	33.8	1.31
47	"	"	0.50	31.0	0.82
48	1140	2	0	27.4	-
49	"	"	0.50	30.4	0.58
50	1250	2	0	23.6	0.42

To determine the influence of the salt present in the calcined stone on the measured reactivity of the calcined dolomite, some samples containing zero NaCl were run in water containing 0.55 gram NaCl per 200 grams of water rather than in distilled water. Figure 6 shows that in the salt solution the measured reactivity was slightly higher than in distilled water.

In comparing the reactivity of calcined dolomite with that of its component oxides, it can be seen that MgO decreases in reactivity very rapidly as the temperature of preparation rises and by 925°C it is very unreactive, while CaO is still very reactive even at the highest temperature employed. Since dolomite is approximately half MgO and half CaO on a molar basis, and the reactivity of the MgO is nearly zero at the temperatures used to decarbonate the dolomite, then it follows that the MgO is acting as a more or less inert diluent and the reactivity is due mainly to the CaO content. One would consequently expect the reactivity of the dolomite to be approximately half that of the CaO. The data confirm this expectation.

Properties of CaO

The properties of CaO prepared by decomposition of CaCO_3 containing various amounts of NaCl are given in table 2.

Figure 7 shows that at the lower temperatures NaCl decreases the surface area to a marked extent. However, at the higher temperatures the influence of salt on the surface area is much less. For comparison purposes the surface areas of calcined Missouri limestone, as determined by Staley and Greenfeld (1949), are included. Above 1050° C there is some agreement; at less than 1050° C the agreement is not as good.

The reactivity values are shown in figures 6 and 8. In figure 8 the surface area was plotted vs. the reactivity, without regard to either the salt content or calcining temperature. It appears as though the surface area of the CaO must be reduced to less than about $1 \text{ m}^2/\text{gram}$ before there is any appreciable decrease in the reactivity. However, beginning at about $1 \text{ m}^2/\text{g}$ the rate of decrease in reactivity becomes very rapid. The reactivity seems to be independent of how the surface area decrease is produced, whether by increase in temperature of preparation or by addition of NaCl.

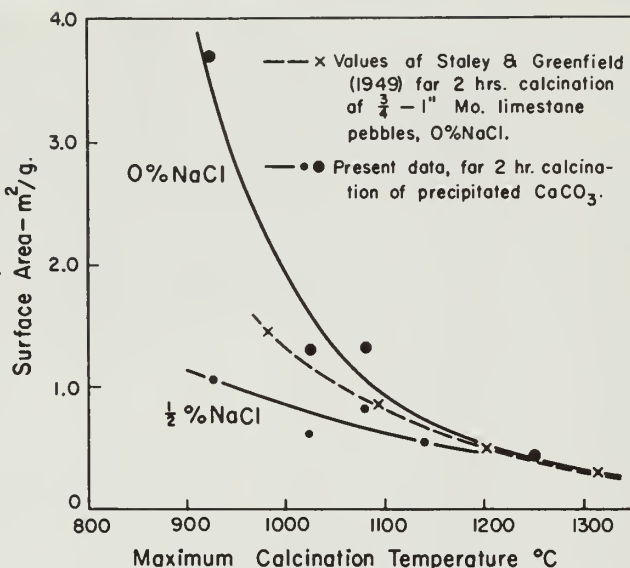
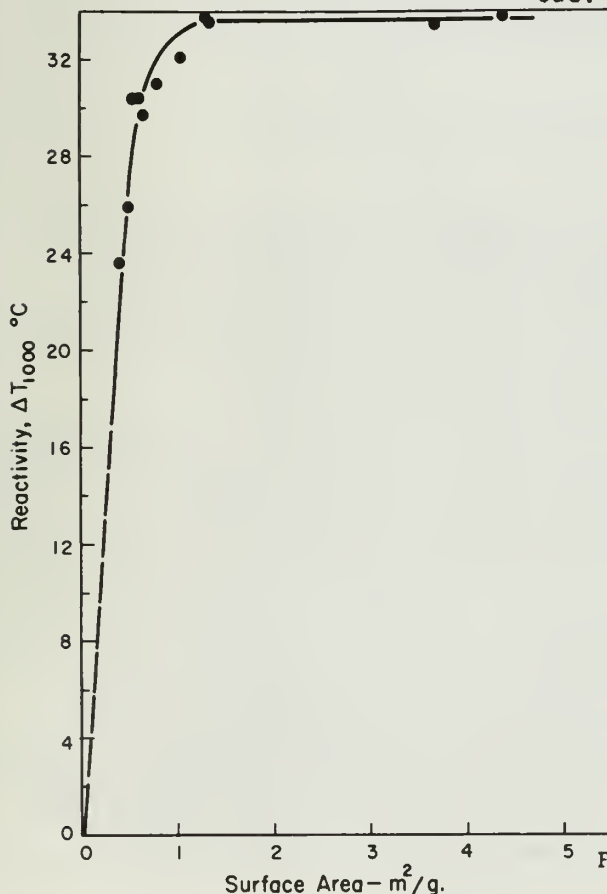


Fig. 7. - Influence of NaCl on the surface area of CaO. Time at maximum temperature was two hours.



Properties of MgO

Some properties of MgO produced by decomposition of the basic magnesium carbonate are given in table 3.

Figure 9 shows that the surface area decreases rapidly as the calcination temperature increases, and that salt decreases the surface area considerably at the lower temperatures, but has a smaller effect at the higher temperatures. Some data of Livey, Wanklyn, Hewitt and Murray (1957) on the surface area of MgO produced by decomposition of $\text{Mg}(\text{OH})_2$ containing no salt are given for comparison. Considering the different starting materials and preparation methods, the agreement is not bad, especially at the higher temperatures.

Figures 6 and 10 show the reactivity of MgO. From figure 10 it appears that the reactivity falls

Fig. 8. - Reactivity of CaO with various surface areas.

Table 3. - Properties of MgO

No.	Maximum calcining temp. (°C)	Total time at max. temp. (hrs.)	NaCl added (wt. % based on unburned basic $MgCO_3$)	Reactivity ΔT_{1000} (°C)	Surface area (m^2 /gram)
51	500	2	0	14.8	104.3
52	"	"	0.5	6.9	78.2
53	625	2	0	1.5	-
54	"	"	0.5	1.1	-
55	720	2	0	0.9	32.85
56	"	"	0.5	0.7	28.08
57	925	2	0	0.3	8.00
58	"	"	0.5	0.3	6.46
59	1250	2	0	0.0	1.44

rather rapidly with a decrease in surface area down to approximately 60 m^2 /gram, then the reactivity falls off slowly with further decrease in surface area. This relationship between surface area and reactivity for MgO is in contrast with that for CaO.

Some Properties of Laboratory Prepared Hydrates

Dolomitic Hydrates

Table 4 includes, in addition to the Emley plasticity values, the amount of water necessary to produce a hydrate putty of standard consistency and the maximum bed temperature (see section on hydration) attained during the atmospheric pressure hydrations. The water content at standard consistency for both high and low pressure hydrates decreases slightly as the salt content increases at a particular temperature. The high-pressure hydrates required 3 to 5 percent more water to form a paste of standard consistency than the low-pressure hydrates.

The bed temperature, in general, decreases with an increase in both calcining temperature and salt content of the raw stone. This agrees with the decrease in reactivity measured in the calorimeter as these two factors increased.

From table 4 it can be seen that on soaking, the plasticity of the high-pressure hydrates changes very little. They develop nearly their maximum plasticity almost immediately on tempering with water. However, the low-pressure hydrates, in most cases, show a marked increase in plasticity on soaking in water.

The plasticity of the high-pressure hydrates reported in table 4 were all produced by hydrating the calcined dolomite at 140 psi (gauge) for 4½ hours with sufficient excess water so that some liquid water was present in the vessel during this period. Before it was realized that the presence of liquid water was necessary to get a high degree of hydration of the MgO in pressure hydration, some work was carried out using essentially dry steam. In one such experiment a steam generator was set up and essentially dry steam at 60 psi (gauge) was delivered to another container holding the calcined dolomite, which was at a temperature

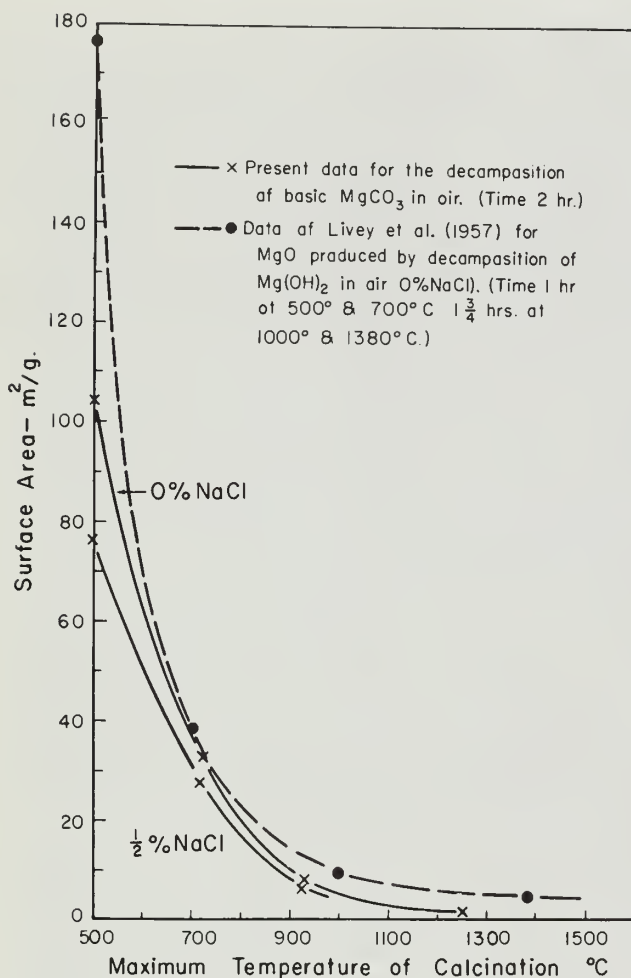


Fig. 9. - Surface area of MgO vs. temperature of preparation.

sufficient to maintain a pressure of 60 psi (guage). After three hours of this treatment the unsoaked plasticity was only 146 and the soaked value was 200. X-ray diffraction patterns showed that very little of the MgO had been hydrated.

Knibbs and Gee (1952), among others, have pointed out the necessity of having liquid water present during pressure hydration in order to effect a high degree of hydration in a short time.

It is evident from table 4, and the above discussion, that the plasticity is strongly dependent upon the method and procedure of hydration, as well as calcining temperature, salt content, soaking, etc.

Table 5 gives surface area values for some of the dolomitic hydrates. The most interesting feature of table 5 is the large increase in the surface area of the low-pressure hydrates upon soaking, and the rather small increase in the area of the high-pressure hydrates. It appears that a more or less extensive interaction of the low-pressure hydrates with water takes place, but that the interaction with the high-pressure hydrates is less extensive. The presence of salt in the raw

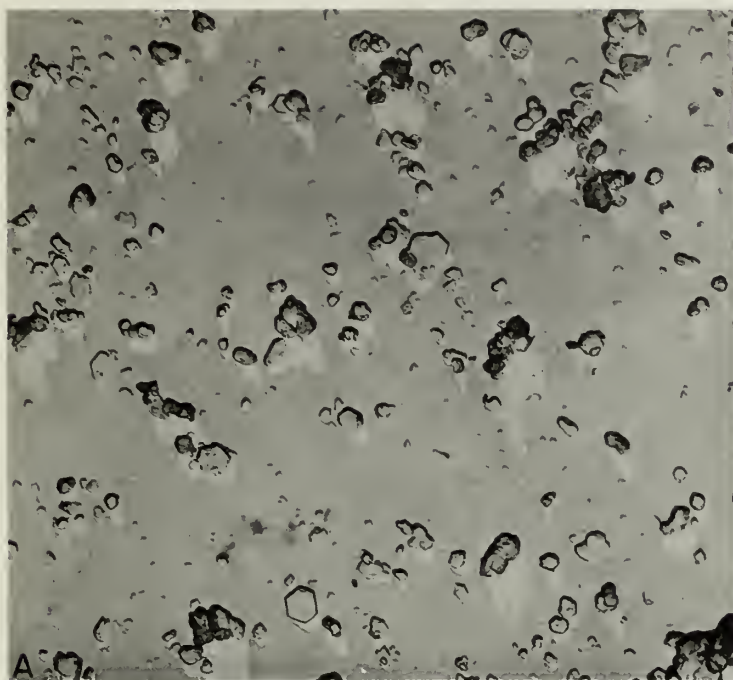
Table 4. - Emley Plasticity Values of Laboratory Prepared Dolomitic Hydrates^a

No.	High-pressure hydration			Low-pressure hydration			Maximum bed temperature (°C)
	Emley plasticity ^b		Water ^c at standard consistency	Emley plasticity ^b		Water ^c at standard consistency	
	Unsoaked	Soaked		Unsoaked	Soaked		
8	326	320	45.3	242	296	41.3	90
9	388	392	42.8	238	309	39.8	85
10	416	455	42.3	198	274	37.1	75
11	434	423	43.1	190	232	38.2	62
12	435	455	42.2	190	238	37.4	55
13	-	-	-	-	-	-	-
14	395	424	44.0	189	217	38.1	67
15	-	-	-	-	-	-	-
16	432	430	43.4	193	245	37.6	62
17	-	-	-	-	-	-	-
18	-	-	-	226	335	40.3	88
19	-	-	-	132	246	38.5	79
20	-	-	-	126	229	38.5	75
21	326	388	44.7	178	250	41.1	81
22	351	424	41.2	-	-	-	-
23	403	408	42.7	-	-	-	-
24	320	353	43.0	150	206	39.0	75
25	304	355	42.2	148	189	35.7	77
26	284	334	41.2	147	173	36.4	78
27	278	277	40.0	131	147	34.9	74
28	346	396	40.5	144	176	34.2	69
29	321	360	39.2	141	199	34.4	68
30	232	261	42.8	128	160	38.9	73
31	255	262	41.2	122	163	36.5	68
32	259	278	41.0	124	152	35.5	64
33	208	203	36.9	-	-	-	-
34	208	206	40.6	-	-	-	-

^a For compositions, calcination temperatures, etc., see table 1.

^b Percent water by weight in standard consistency paste.

^c Soaking period 24 hours.



ELECTRON MICROGRAPHS

A — Magnesium hydroxide crystals

B — Calcium hydroxide crystals

Magnification approximately 20,000 diameters

Table 5. - Surface Area of Laboratory Prepared Dolomitic Hydrates (meters²/gram)^a

No.	<u>High-Pressure Hydration</u>		<u>Low-Pressure Hydration</u>	
	Unsoaked	Soaked	Unsoaked	Soaked
8	12.37	-	14.04	-
9	-	-	-	-
10	-	-	-	-
11	12.88	-	11.09	-
12	-	-	-	-
13	-	-	-	-
14	-	-	-	-
15	-	-	-	-
16	-	-	-	-
17	-	-	-	-
18	-	-	14.46	24.47
19	-	-	11.25	27.55
20	-	-	10.95	-
21	13.04	14.65	12.96	23.55
22	11.90	-	-	-
23	14.90	-	-	-
24	10.81	11.90	10.68	26.71
25	10.05	12.30	9.48	22.35
26	9.67	11.32	8.20	19.47
27	-	-	-	-
28	-	-	-	-
29	-	-	-	-
30	9.52	11.53	9.61	22.69
31	9.12	10.84	9.28	17.66
32	9.18	10.28	9.40	16.53
33	11.44	-	-	-
34	9.54	-	-	-

^a For compositions, calcination temperatures, etc., see table 1.

stone or the increase in calcining temperature, in general, results in decreased surface area of both the high- and low-pressure hydrates. Another interesting result is that the surface areas of the unsoaked, high- and low-pressure hydrates are very nearly identical for the same temperature of preparation and the same salt content.

Figures 11, 12 and 13 show the relationships between the surface area and the Emley plasticity for unsoaked and for soaked dolomitic hydrates produced by high- and low-pressure hydration.

Figure 11 shows that for the high-pressure hydrates there is an increase in plasticity as the surface area of the hydrates increases. The same relationship holds for both soaked and unsoaked values.

In figure 12, for the low-pressure hydrates, there is considerable scatter, but there appears to be a relationship between surface area and plasticity, and the plasticity increases with the surface area. It will be noticed that the soaked specimens have higher surface areas than the unsoaked.

In figure 13 the plasticity-surface area relationship for high- and low-pressure hydrates in the unsoaked condition is compared directly. It appears that the rate of increase of plasticity with increasing surface area is greater for high-pressure hydrates than for low-pressure hydrates. Even though both the high- and low-pressure hydrates have nearly the same surfaces, the high-pressure hydrates are usually more plastic.

Bishop (1939) calculated the surface area from particle size distribution curves for a number of commercial hydrates and compared them with the Emley plasticity values. He stated that no relationship existed between plasticity and surface area or particle size distribution of hydrates. This is at variance with the present data shown in figures 11, 12, and 13, which strongly suggest that a relationship does exist between surface area and plasticity. Bishop further stated that the lack of correlation may have been due to the fact that he could not determine the size distribution of particles of less than 2 microns and that these particles may have a large influence on plasticity. He showed that the plasticity of fractions finer than 2 microns from highly plastic hydrates was very great but similar fractions from low plasticity hydrates were not very plastic. The method of surface area determination used here measured the surface area of the entire sample and not just a fraction of it, as was the case in Bishop's method.

Also, an examination of figures 11, 12, and 13 shows that the relationship between surface area and plasticity depends on the method of hydration and the subsequent treatment of the hydrates. The relationship would probably break down if one tried to relate various hydrates with no knowledge of their preparation and pretreatment. This is what Bishop did and may be a part of the reason for his findings.

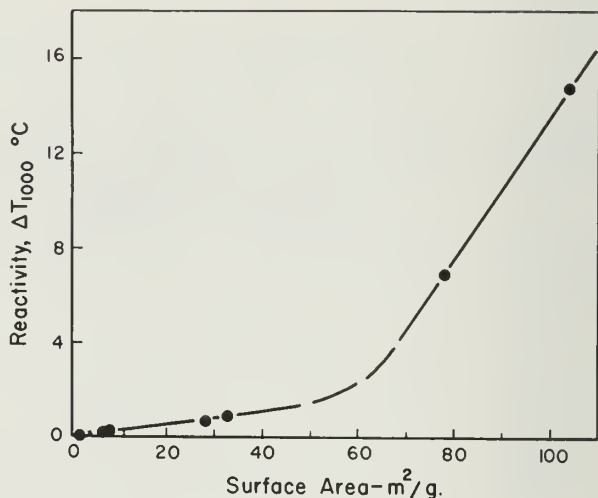


Fig. 10. - Reactivity of MgO vs. surface areas.

Tables 6 and 7 give the compositions of the hydrates as determined from the ignition loss and also some CO_2 contents.

During soaking the hydrates pick up some CO_2 , but the total amount in the samples is less than 1 percent. For the samples on which the CO_2 content was determined, the compositions calculated from the ignition losses were corrected for the CO_2 picked up. The correction was very small. This fact gives us confidence that the compositions calculated from the ignition loss data are roughly correct.

Table 6 indicates that the high-pressure hydrates are all very nearly completely hydrated regardless of the calcining temperature or salt content of the raw stone. Furthermore, on soaking there is no significant increase in $\text{Mg}(\text{OH})_2$ content.

Table 7 shows that the low-pressure hydrates are far from being completely hydrated. However, lower calcining temperatures and salt contents seem to favor a slightly greater degree of hydration. In most cases soaking of these hydrates appears to increase the degree of hydration, especially at lower salt contents. The proportion of $\text{Ca}(\text{OH})_2$ in the low-pressure hydrates appears to be larger than in the high-pressure hydrates.

From compositions given in tables 6 and 7, the percentage of the total possible $\text{Mg}(\text{OH})_2$ was calculated. This was then plotted vs. the unsoaked

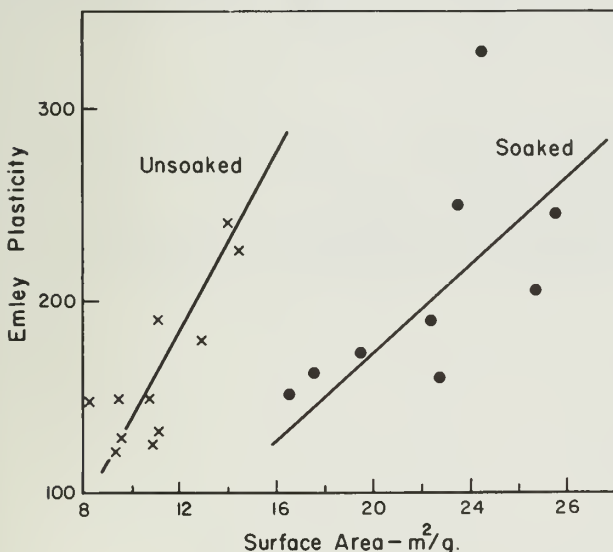


Fig. 12. - Surface area of low-pressure dolomitic hydrates vs. Emley plasticity.

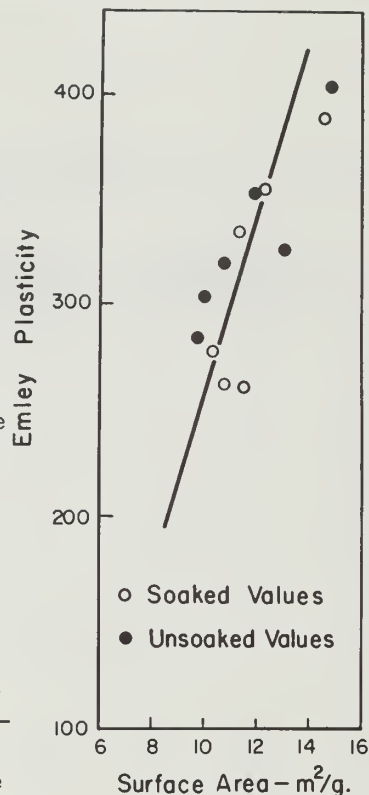


Fig. 11. - Surface area of high-pressure dolomitic hydrates vs. Emley plasticity.

Emley plasticity values, as shown in figure 14. It will be noted that the plasticity increases with increases in the amount of $\text{Mg}(\text{OH})_2$. As the calcining temperature rises, the plasticity decreases, even when very nearly all the possible $\text{Mg}(\text{OH})_2$ is present.

This indicates that increased amounts of $\text{Mg}(\text{OH})_2$ produce better plasticity, and that any way of producing $\text{Mg}(\text{OH})_2$ from the MgO in the calcined Thornton, Illinois, dolomite will improve the plasticity.

All indications are that the presence of $\text{Mg}(\text{OH})_2$ improves the plasticity. In the hope of throwing more light on the reasons for

Table 6. - Composition of Laboratory Prepared High-Pressure Hydrated Dolomitic Limes^a (Calculated from Ignition Loss)^b

No.	Ignition Loss (%)		Composition (%)						CO ₂ Content (%)	
	Unsoaked	Soaked	Unsoaked			Soaked			Unsoaked	Soaked
			Ca(OH) ₂	Mg(OH) ₂	MgO	Ca(OH) ₂	Mg(OH) ₂	MgO		
8	25.7	-	57.0	38.2	4.8	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-
11	27.0	-	56.0	43.0	1.0	-	-	-	-	-
12	-	-	-	-	-	-	-	-	-	-
13	-	-	-	-	-	-	-	-	-	-
14	-	-	-	-	-	-	-	-	-	-
15	-	-	-	-	-	-	-	-	-	-
16	-	-	-	-	-	-	-	-	-	-
17	-	-	-	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-	-	-	-
21	26.5	26.6	56.4	41.2	2.4	56.3	41.5	2.2	-	-
22	25.4	-	57.3	36.7	6.0	-	-	-	-	-
23	27.1	-	56.0	43.4	0.6	-	-	-	-	-
24	26.0	26.4	56.8	39.2	4.0	56.6	40.0	3.4	0.218	0.772
25	25.7	25.9	57.0	38.1	4.9	56.8	38.8	4.4	-	-
26	26.1	26.2	56.7	39.6	3.7	56.6	40.0	3.4	-	-
27	-	-	-	-	-	-	-	-	-	-
28	-	-	-	-	-	-	-	-	-	-
29	-	-	-	-	-	-	-	-	-	-
30	25.7	26.2	57.0	37.8	5.2	56.8	39.3	3.9	0.216	0.761
31	25.7	26.1	57.0	37.8	5.2	56.7	39.6	3.7	-	-
32	26.0	26.1	56.8	39.2	4.0	56.7	39.7	3.6	-	-

a For compositions, calcination temperatures, etc., see table 1.

b See "Experimental Procedure."

Table 7.- Composition of Laboratory Prepared Low-Pressure Hydrated Dolomitic Limes^a (Calculated from Ignition Loss)^b

No.	Ignition Loss (%)		Composition (%)						CO ₂ Content (%)	
	Unsoaked	Soaked	Unsoaked			Soaked			Unsoaked	Soaked
			Ca(OH) ₂	Mg(OH) ₂	MgO	Ca(OH) ₂	Mg(OH) ₂	MgO		
8	16.2	-	64.1	1.9	34.0	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-
11	17.8	-	62.9	8.1	29.0	-	-	-	-	-
12	-	-	-	-	-	-	-	-	-	-
13	-	-	-	-	-	-	-	-	-	-
14	-	-	-	-	-	-	-	-	-	-
15	-	-	-	-	-	-	-	-	-	-
16	-	-	-	-	-	-	-	-	-	-
17	-	-	-	-	-	-	-	-	-	-
18	16.4	19.2	64.0	2.6	33.4	61.9	13.6	24.5	-	-
19	16.7	19.5	63.7	3.9	32.4	61.6	14.6	23.8	-	-
20	16.9	-	63.6	4.5	31.9	-	-	-	-	-
21	16.3	19.1	64.0	2.4	33.6	61.9	13.0	25.1	-	-
22	-	-	-	-	-	-	-	-	-	-
23	-	-	-	-	-	-	-	-	-	-
24	16.2	19.4	64.2	1.5	34.3	61.8	13.4	24.8	0.262	0.765
25	15.8	16.7	64.4	0.4	35.2	63.8	3.4	32.8	-	0.712
26	15.9	16.3	64.3	0.9	34.8	64.0	2.3	33.7	-	-
27	-	-	-	-	-	-	-	-	-	-
28	-	-	-	-	-	-	-	-	-	-
29	-	-	-	-	-	-	-	-	-	-
30	15.5	19.0	64.6	0	35.4	62.4	11.8	25.8	0.304	0.811
31	15.8	18.1	64.6	0	35.4	62.8	8.4	28.8	0.331	0.861
32	15.6	16.9	64.6	0	35.4	63.7	4.4	31.9	-	-

a For compositions, calcination temperatures, etc. see table 1.

b See "Experimental Procedure."

this, particle size distributions were determined on three samples containing different amounts of $Mg(OH)_2$ produced by different methods of hydration and soaking.

The three samples investigated were all derived from the calcinate from run No. 24 by the following treatments:

- A) Low-pressure hydrated, unsoaked.
- B) Low-pressure hydrated, soaked.
- C) High-pressure hydrated, unsoaked.

Figure 15 shows the particle size distribution of these three samples. If we consider the region of less than one micron, it appears that C has the greatest amount of fine material, followed next by B, and that A has the least amount. On comparing their plasticity values, C has the highest plasticity (320), followed by B (206), and then A (150). It appears that the samples with the greatest amount of fine material had the highest plasticities.

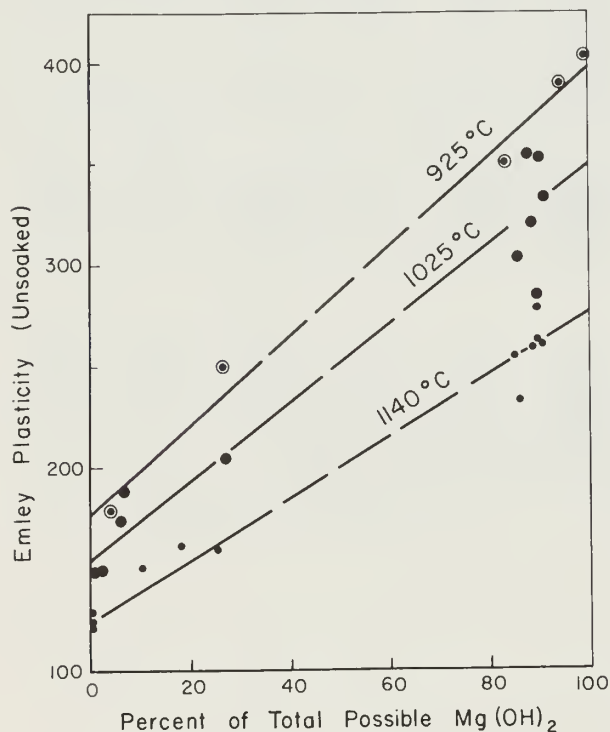


Fig. 14. - Emley plasticity vs. percentage of total possible $Mg(OH)_2$ for various maximum temperatures of calcination.

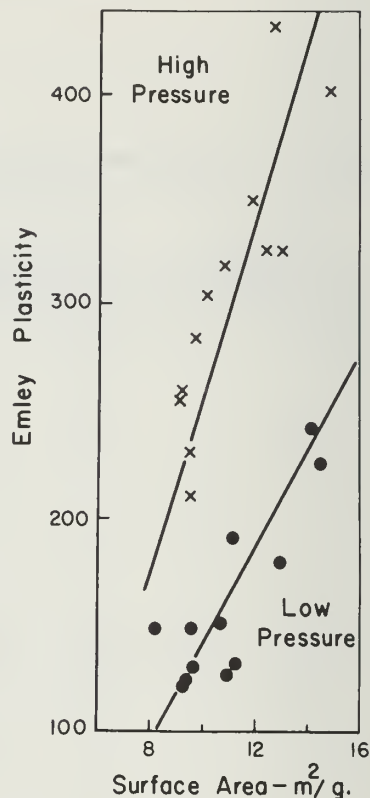


Fig. 13. - Comparison of high- and low-pressure dolomitic hydrates, both unsoaked.

Now if one considers the $Mg(OH)_2$ content (tables 6 and 7) it is seen that it increases as the plasticity increases, or C contains the most and A the least $Mg(OH)_2$, with B intermediate.

Inasmuch as larger amounts of fine material are associated with higher $Mg(OH)_2$ contents, then the $Mg(OH)_2$ should tend to be a fine material. To check this, x-ray diffraction patterns of various size fractions were made. The results are summarized in table 8, from which it appears that the proportion of $Mg(OH)_2$ steadily increases in the finest fractions of B and C.

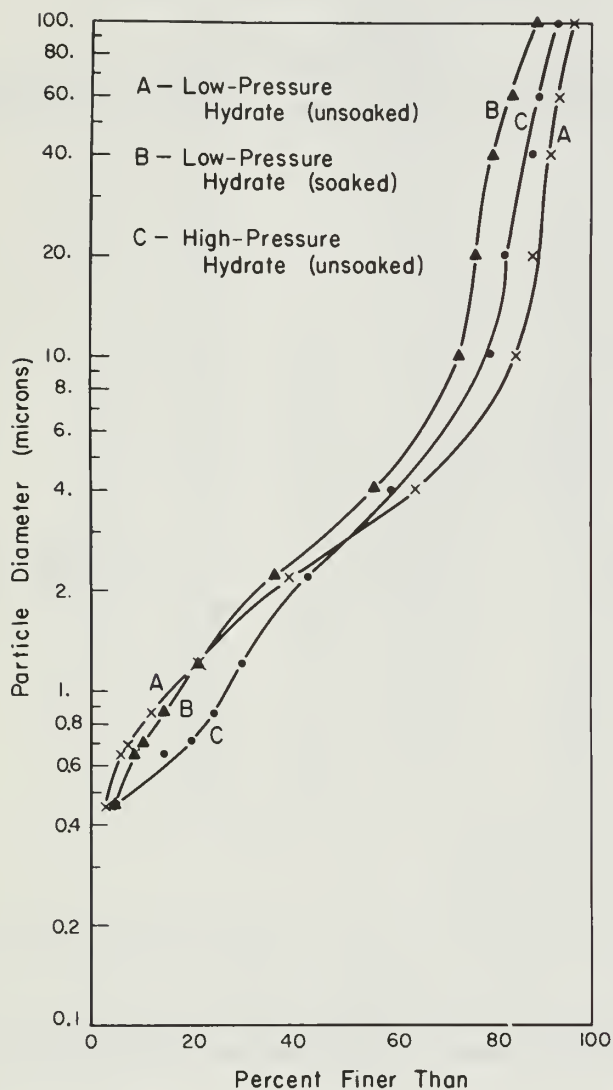


Fig. 15. - Particle size distribution of laboratory-prepared dolomitic hydrate No. 24.

Table 8. - X-Ray Identification and Intensity of Certain Lines for Laboratory-Prepared Dolomitic Hydrates

Hydrate	Size fraction (microns)	Intensity of X-ray Lines (cm above background)				Ratio	
		(1)*	(2)	(3)	(4)	Int. $Mg(OH)_2$	(18.5°)
		$Ca(OH)_2$	$Mg(OH)_2$	$Mg(OH)_2$	MgO	Int. $Ca(OH)_2$	(18.0°)
No. 24 Low-pressure hydration (unsoaked) (Sample A)	4	4.6	0	0	7.5	0	
	2.2	4.7	0	0	9.3	0	
	1.2	5.1	0	0	11.0	0	
	0.86	4.6	0	0	10.7	0	
	0.70	4.6	0	0	9.7	0	
	0.62	4.6	0	0	8.5	0	
No. 24 Low-pressure hydration (soaked) (Sample B)	20	7.5	2.1	1.6	7.0	0.28	
	4	7.5	2.0	1.6	8.3	0.27	
	2.2	7.6	2.6	1.6	7.3	0.34	
	1.2	6.7	2.4	1.9	8.6	0.36	
	0.86	6.6	2.9	2.1	9.0	0.44	
	0.70	5.7	3.0	2.9	10.3	0.53	
	0.62	5.3	3.1	2.1	8.6	0.58	
	0.46	5.2	2.7	1.6	7.4	0.52	
No. 24 High-pressure hydration (unsoaked) (Sample C)	60	8.4	4.7	4.5	1.0	0.56	
	20	8.7	5.6	4.7	0.9	0.64	
	4	9.3	5.8	5.9	0.6	0.62	
	2.2	9.8	7.2	7.0	1.2	0.74	
	1.2	9.6	9.3	8.3	1.0	0.95	
	0.86	9.6	10.9	10.3	1.3	1.14	
	0.70	7.3	9.8	10.1	0.8	1.34	
	0.62	5.2	9.3	8.8	0.5	1.79	
	0.46	4.5	8.5	8.7	0.3	1.89	

*(1) $Ca(OH)_2$ line at 18.0° in 2 θ

(2) $Mg(OH)_2$ line at 18.5° in 2 θ

(3) $Mg(OH)_2$ line at 37.8° in 2 θ

(4) MgO line at 42.8° in 2 θ

From this discussion it seems likely that the reason for the increase in plasticity as the $Mg(OH)_2$ increases is that the $Mg(OH)_2$ forms as very fine particles.

Bishop (1939) observed that the fractions less than 2 microns from highly plastic limes were very plastic, but that the same fractions from low plasticity limes were not plastic. This can now be explained from the above data; that is, the high plasticity limes have greater amounts of very fine material which is richer in $Mg(OH)_2$ than the nonplastic hydrates.

$Mg(OH)_2$ and $Ca(OH)_2$

Some of the MgO samples previously discussed (table 3) were pressure hydrated by the usual procedure (140 psi for 4½ hours), then the surface area and plasticity was measured. The results are given in table 9.

Table 9. - Some Properties of $\text{Mg}(\text{OH})_2^a$

No.	Emley plasticity		Water at standard consistency (%)	Surface area (m^2/gram)	
	Unsoaked	Soaked		Unsoaked	Soaked
55	645	625	63.8	36.65	-
57	468	480	50.0	12.85	17.52
58	400	410	50.2	-	-
59	468	468	43.5	7.78	-

a For compositions, calcination temperatures, etc., see table 3.

 Table 10. - Some Properties of $\text{Ca}(\text{OH})_2^a$

No.	Emley plasticity		Water at standard consistency (%)	Surface area (m^2/gram)	
	Unsoaked	Soaked		Unsoaked	Soaked
42	101	93	54.5	7.37	7.84
44	172	102	47.9	7.04	-
45	173	71	46.2	-	-
50	202	246	44.0	11.84	-

a For compositions, calcination temperatures, etc., see table 2.

The plasticity, surface area, and water content at standard consistency for No. 55, prepared from MgO formed at 720°C , are very high. As the temperature of preparation of the MgO rises to 925°C , the plasticity, surface area, and water necessary to form a paste of standard consistency decrease. The presence of salt seems to decrease the plasticity somewhat. The MgO formed at 1250°C produced a hydrate of approximately the same plasticity as that produced from MgO prepared at 925°C , both without salt.

Some of the CaO samples given in table 2 were pressure-hydrated by the usual procedure, then the surface area and plasticity were measured. The results are given in table 10.

The unsoaked and soaked plasticities are all rather low. The increase in both the soaked and unsoaked plasticities as the temperature of preparation of the CaO increases is unexpected, and no explanation is apparent at present.

The particle size distribution of pressure-hydrated $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, prepared from their respective oxides, which were formed at 925°C , are given in figure 16. It will be noticed that the $\text{Mg}(\text{OH})_2$ has a much larger proportion of fine material (less than 2μ) than the $\text{Ca}(\text{OH})_2$. If we compare the plasticities (tables 9 and 10), it is apparent that $\text{Mg}(\text{OH})_2$ is much more plastic than $\text{Ca}(\text{OH})_2$.

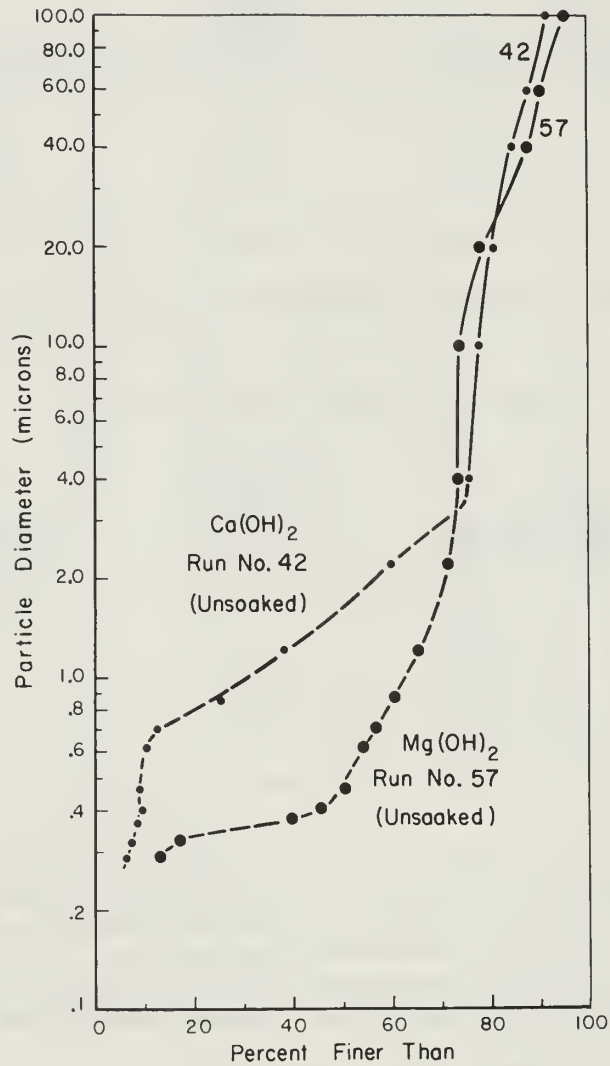


Fig. 16. - Particle size distribution of Ca(OH)_2 and Mg(OH)_2 prepared by pressure hydration.

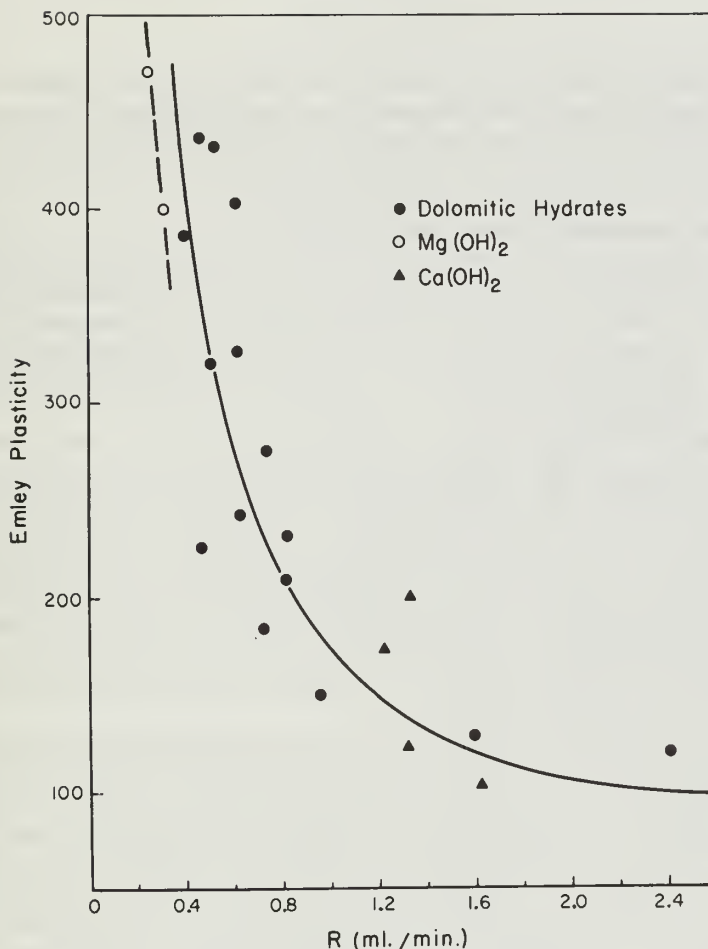


Fig. 17. - Water removal factor R vs. Emley plasticity.

Electron micrographs of the same samples that were used for the particle size distribution are shown in plate 1.

It is evident once again that the $\text{Mg}(\text{OH})_2$ contains more fine crystals than the $\text{Ca}(\text{OH})_2$. In both cases, however, many of the particles are rather thin hexagonal platelets.

The water removal factor, R (see fig. 3 and section on water retention of hydrates), in relation to the plasticity is shown in figure 17. It will be noted that the fine particle sized samples (as $\text{Mg}(\text{OH})_2$) show a low rate of water removal and high plasticities, but that the larger particle sized $\text{Ca}(\text{OH})_2$ shows a lower plasticity and relatively high water removal rates. The dolomitic hydrates lie between these two extremes and their position probably depends mainly on the proportion of $\text{Mg}(\text{OH})_2$ present in the hydrate.

DISCUSSION

It has been demonstrated by experimental data that the presence of NaCl decreases the reactivity and surface area of calcined dolomite, CaO and MgO. Noda (1938, 1939) has shown that the presence of NaCl in limestone or magnesite caused increased grain growth and decreased reactivity of the CaO and MgO formed on calcination of the carbonates. Atlas (1957) has shown that the lithium halides also catalyze the sintering or grain growth of MgO.

Staley and Greenfeld (1947) observed that limes prepared from limestones to which 0.5 percent NaCl had been added had low surface areas and that the sodium chloride apparently acted as a fluxing material, increasing the mobility of the calcium and oxygen ions sufficiently to permit them to pack more rapidly than in its absence. Noda and Kan (1937) also found that the addition of NaCl accelerated crystal growth of CaO.

Tacvorian (1952, 1954) has suggested a mechanism by which the surfaces of refractory oxide grains may be activated and thus cause an acceleration of the sintering process. He believed that if the refractory oxide is mixed and heated with a compound which is a weakened model, a relatively concentrated solid solution may be formed in the surface of the refractory grain. The surface solid solution will have lower activation energies and therefore higher ionic diffusion rates than the pure refractory oxide. This increase in the ionic diffusion rate causes crystal growth to occur at a greater rate, since at the point of contact of two small crystals the atoms of the two crystals interdiffuse more readily and the net result is the production of a larger crystal.

The application of Tacvorian's ideas to the systems NaCl-CaO and NaCl-MgO would require NaCl to be a weakened model of CaO and MgO. Especially for the MgO, due to the large difference in size of the Mg^{++} and Na^{+} ions, it is not easy to think of NaCl as such a model. However, Atlas (1957) showed that although LiCl and LiBr were not truly weakened models of MgO (due to the discrepancy between the radii of Cl^{-} and Br^{-} and O^{--} ions), they were nevertheless as effective in catalyzing the sintering of MgO as was the true weakened model, LiF. To him this suggested the importance of the cation, since in the three halides the cation was the same. He suggests that the Li^{+} ion from the chloride and bromide can be incorporated into the surface layer of MgO and that this solution may be aided by partial thermal decomposition of the halide to Li_2O . Since Li_2O does not have the same cation to anion ratio as MgO, solution of Li_2O in MgO must be accompanied by the formation of defects, as either O^{--} vacant sites or interstitial Li^{+} ions. Such defects will increase the rate of diffusion or material transport and thereby the sintering or grain growth rate.

If one applies these ideas, then in the case of CaO, the Ca^{++} and Na^{+} ions are nearly the same size, and if some of the NaCl is partially thermally decomposed, then the Na_2O could go into solution in the surface of the CaO crystals and cause defects, which will increase the rate of diffusion and promote sintering of the CaO. However, in the case of MgO there is such a large difference in the radii of Mg^{++} and Na^{+} ions that if the above conceptions of the mechanism of promotion of sintering are valid, then Na^{+} should not be an effective aid in the promotion of sintering of MgO. If one uses the surface area as a measure of grain growth, then from figures 7 and 9 it can be seen that NaCl causes a greater decrease in the surface area of CaO than in the surface area of MgO when compared on a percentage basis. So in dolomite the influence of NaCl on grain growth should be the greatest for the CaO.

Fig. 18. - Emley plasticity of low-pressure hydrates made from calcined dolomite from Thornton, Illinois, vs. reactivity (see "Experimental Procedures") of the calcinates.

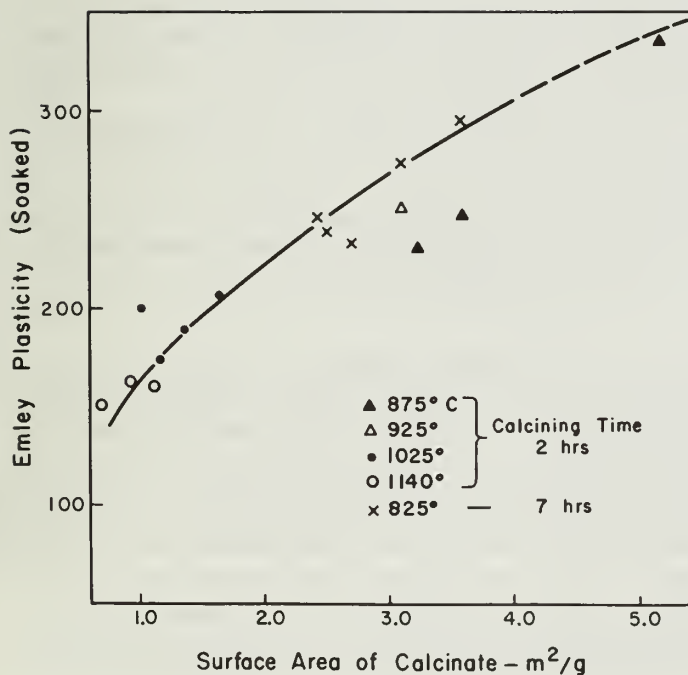
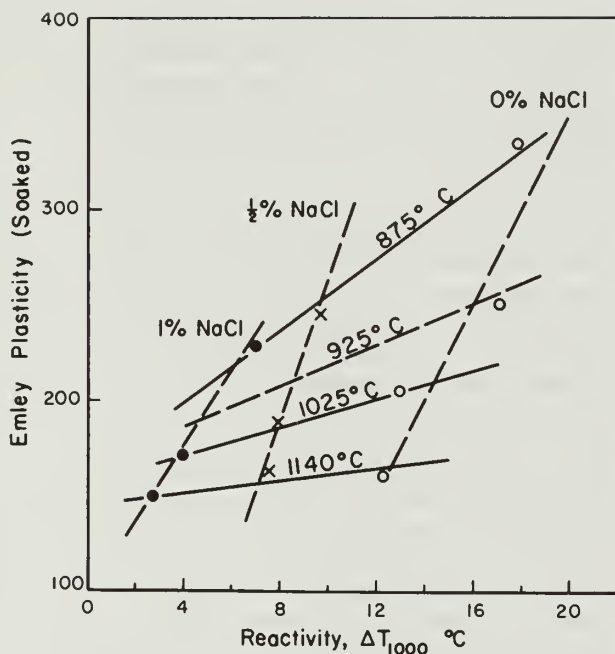


Fig. 19. - Emley plasticity of low-pressure hydrated calcined dolomite from Thornton, Illinois, vs. the surface area of the calcinate.

The over-all effect of NaCl on the oxides appears to be the same as the effect of thermal treatment. That is, it promotes sintering. A small amount of NaCl will affect sintering to about the same degree as a small increase in temperature.

Next one must consider what influence the NaCl enhanced growth of the oxide crystallites has on the properties of the hydrates, particularly the plasticity. Because the plasticity depends strongly on the method of hydration, the results given are relative and may not apply to methods other than those used here. To this end consider the data in figures 18, 19, and 20, which show correlations between the oxide properties and plasticity of the hydrates.

In the case of low-pressure hydration, figure 18 shows that at any given temperature the plasticity decreases as the salt content rises. So the decrease in the reactivity of the oxide, produced by NaCl-enhanced sintering, results in a less plastic hydrate when low-pressure hydration is used.

Figure 19 shows that as the surface area of the oxides, derived from calcining dolomite, decreases (no distinction being made between the effect of salt and temperature of calcination), the plasticity of the low-pressure hydrates also decreases.

Figure 20 shows that for the high-pressure hydrates the plasticity of the hydrate is increased by the addition of salt to the raw stone at all surface areas, especially at the higher surface areas.

In the low-pressure hydrates, the presence of salt during calcination does not increase the plasticity. Salt appears to help produce a more plastic lime in high-pressure hydrates, but even the least plastic pressure-hydrated lime is of such a high plasticity that increasing it further by adding salt seems to be of questionable value.

The results of Briscoe and Mathers (1927) seem to be somewhat at odds with the present results. This may be due to different stones, different hydration methods, different calcining procedures, etc., none of which they described. They stated that pressure hydration produces low plasticity hydrates and that the addition of salt to their dolomite produced a highly plastic hydrate by low-pressure hydration. In their conclusions they stated that "the plastic properties of hydrated limes seem to be determined by the extent to which hydration progresses during the soaking of the lime to form putty. If the lime is completely hydrated at the time of formation of the dry product, it will be a non-plastic lime. The quicklime must be produced so that during hydration the CaO hydrates slowly, but yet the MgO is reactive and on soaking the MgO will hydrate extensively and produce a highly

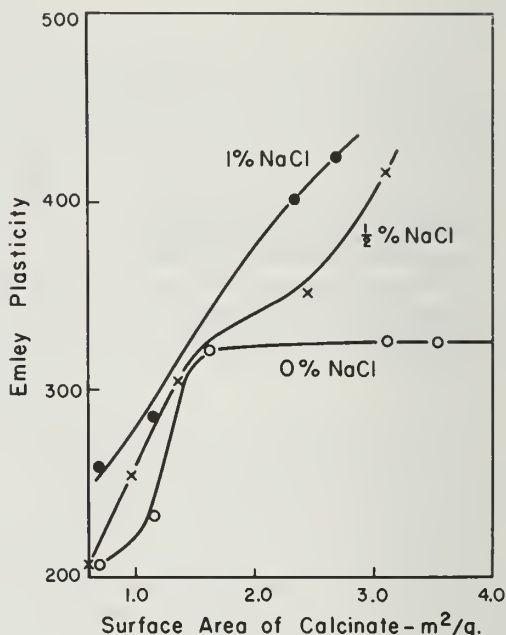


Fig. 20. - Emley plasticity of high-pressure hydrated calcined dolomite from Thornton, Illinois, vs. the surface area of the calcinate.

plastic lime." They believed that salt decreases the activity of the CaO and not that of the MgO so that on low-pressure hydration the CaO hydrates slowly, leaving the MgO unhydrated but yet reactive, and on soaking the hydrate a high plasticity results due to the hydration of the MgO.

The present information seems to confirm Briscoe and Mathers' (1927) conclusion that the influence of salt on the sintering of CaO is greater than it is on MgO. There seems to be agreement that the plasticity is greatly increased in dolomitic hydrates if most of the MgO is converted to Mg(OH)_2 . However, the present data indicate that the method of conversion has little influence.

Webb and Sampson (1957) and a number of patents by Corson (Corson, 1946) show the great increase in plasticity produced by pressure hydration in which a high proportion of the MgO is converted to Mg(OH)_2 .

This brings us to a consideration of plasticity itself. As already shown, the presence of increased amounts of Mg(OH)_2 in dolomitic hydrates increases the plasticity, whether the Mg(OH)_2 is formed by pressure hydration of the oxides or by soaking a low-pressure hydrate. It was further demonstrated that Mg(OH)_2 is very finely divided compared to Ca(OH)_2 and that it has, in the pure state, a much higher plasticity than Ca(OH)_2 . Electron micrographs indicate that both pure Mg(OH)_2 and Ca(OH)_2 , pressure-hydrated, are thin hexagonal platelets. Also the Mg(OH)_2 tends to retain its water with greater tenacity than Ca(OH)_2 or a mixture of Ca(OH)_2 and MgO such as exists in partly hydrated dolomitic limes.

The greater ability of the lime putty to retain its tempering water is important, since in the Emley plasticimeter, water is being removed by the porous base plate and the more slowly this water is removed the greater will be the plasticity figure.

Since Ca(OH)_2 and Mg(OH)_2 have the same particle shape (pl. 1), one is led to believe that the large difference in their plasticity is, to a considerable extent, due to the smaller crystal size of Mg(OH)_2 as compared to Ca(OH)_2 .

The rate of withdrawal of water from the putty on the Emley apparatus is a capillary phenomenon in which the capillaries in the putty tend to resist the withdrawal. Small particles make for small capillaries and therefore greater resistance to water removal.

It appears that any situation which will promote the conversion of the free MgO in calcined dolomites to Mg(OH)_2 will increase the plasticity of the lime produced. This is believed to be due to the fine particle size of the Mg(OH)_2 which tends to increase the ability of the putty to retain water.

CONCLUSIONS

1) The addition of salt to dolomite before calcining in the manner described, and then hydrating this calcined dolomite at low pressures by the method described, does not increase the plasticity of the lime produced. NaCl appears to increase slightly the plasticity of the pressure-hydrated dolomitic limes.

2) Mg(OH)_2 is considerably finer than Ca(OH)_2 produced under the same conditions. Both show thin, hexagonal platelets at high magnification. The Mg(OH)_2 retains water much better than Ca(OH)_2 and shows a higher Emley plasticity.

3) Any method used in this investigation (such as soaking at atmospheric pressure or pressure hydration of the calcined dolomite) that increased the amount of Mg(OH)_2 also resulted in increased plasticity of the lime.

4) The results of this work indicate that, in general, the method of manufacture of the hydrate is more important than the presence of NaCl, as far as the production of high plasticity is concerned.

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